NEGATIVE POISSON'S RATIO MATERIAL-CONTAINING CMP POLISHING PAD

FIELD OF THE INVENTION

[0001] This invention pertains to polishing pads for use in chemical-mechanical polishing.

BACKGROUND OF THE INVENTION

[0002] Chemical-mechanical polishing ("CMP") processes are used in the manufacturing of microelectronic devices to form flat surfaces on semiconductor wafers, field emission displays, and many other microelectronic workpieces. For example, the manufacture of semiconductor devices generally involves the formation of various process layers, selective removal or patterning of portions of those layers, and deposition of yet additional process layers above the surface of a semiconducting workpiece to form a semiconductor wafer. The process layers can include, by way of example, insulation layers, gate oxide layers, conductive layers, and layers of metal or glass, etc. It is generally desirable in certain steps of the wafer process that the uppermost surface of the process layers be planar, i.e., flat, for the deposition of subsequent layers. CMP is used to planarize process layers wherein a deposited material, such as a conductive or insulating material, is polished to planarize the wafer for subsequent process steps.

[0003] In a typical CMP process, a wafer is mounted upside down on a carrier in a CMP tool. A force pushes the carrier and the wafer downward toward a polishing pad. The carrier and the wafer are rotated above the rotating polishing pad on the CMP tool's polishing table. A polishing composition (also referred to as a polishing slurry) generally is introduced between the rotating wafer and the rotating polishing pad during the polishing process. The polishing composition typically contains a chemical that interacts with or dissolves portions of the uppermost wafer layer(s) and an abrasive material that physically removes portions of the layer(s). The wafer and the polishing pad can be rotated in the same direction or in opposite directions, whichever is desirable for the particular polishing process being carried out. The carrier also can oscillate across the polishing pad on the polishing table.

[0004] Polishing pads used in chemical-mechanical polishing processes are manufactured using both soft and rigid pad materials, which include polymer-impregnated fabrics, microporous films, cellular polymer foams, non-porous polymer sheets, and sintered thermoplastic particles. A pad containing a polyurethane resin impregnated into a polyester non-woven fabric is illustrative of a polymer-impregnated fabric polishing pad. Microporous polishing pads include microporous urethane films coated onto a base material, which is often an impregnated fabric pad. These polishing pads are closed cell,

porous films. Cellular polymer foam polishing pads contain a closed cell structure that is randomly and uniformly distributed in all three dimensions. Non-porous polymer sheet polishing pads include a polishing surface made from solid polymer sheets, which have no intrinsic ability to transport slurry particles (see, for example, U.S. Patent 5,489,233). These solid polishing pads are externally modified with large and/or small grooves that are cut into the surface of the pad purportedly to provide channels for the passage of slurry during chemical-mechanical polishing. Such a non-porous polymer polishing pad is disclosed in U.S. Patent 6,203,407, wherein the polishing surface of the polishing pad comprises grooves that are oriented in a way that purportedly improves selectivity in the chemical-mechanical polishing. Sintered polishing pads comprising a porous open-celled structure can be prepared from thermoplastic polymer resins. For example, U.S. Patents 6,062,968 and 6,126,532 disclose polishing pads with open-celled, microporous substrates, produced by sintering thermoplastic resins.

[0005] Although several of the above-described polishing pads are suitable for their intended purpose, a need remains for other polishing pads that provide effective planarization, particularly in workpieces polished by chemical-mechanical polishing. In addition, there is a need for polishing pads having longer pad life with improved tear and abrasion resistance properties. There also is a need for polishing pads with improved polishing uniformity that minimize the number of defects, such as edge-on effects and dishing, produced during workpiece polishing.

[0006] The invention provides such a polishing pad. These and other advantages of the invention, as well as additional inventive features, will be apparent from the description of the invention provided herein.

BRIEF SUMMARY OF THE INVENTION

[0007] The invention provides a polishing pad for use in chemical-mechanical polishing systems comprising a material with a Poisson's ratio of less than zero. The invention further provides a method of polishing a workpiece comprising (i) providing a workpiece to be polished, (ii) contacting the workpiece with a chemical-mechanical polishing system comprising the polishing pad of the invention, and (iii) abrading at least a portion of the surface of the workpiece with the polishing system to polish the workpiece.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The invention is directed to a chemical-mechanical polishing pad comprising a porous polymeric material, wherein the porous polymeric material has a Poisson's ratio less than 0. The Poisson's ratio is the ratio of lateral contraction strain to longitudinal strain.

The Poisson's ratio (υ) is related to bulk modulus (B), Young's modulus (E), and shear modulus (G) by the following relationships:

$$B = 2G\,(1 + \upsilon)/3(1 - 2\,\upsilon);$$

$$G = E/2(1 = \upsilon); \text{ and}$$

$$B = E/3(1 - 2\,\upsilon).$$

[0009] When the Poisson's ratio is +1/2, as in rubbery solids, the bulk modulus is much greater than the shear modulus, and the material is incompressible. When the Poisson's ratio is –1, the material is highly compressible but difficult to shear because the bulk modulus and Young's modulus are much greater than the shear modulus. A material having a negative Poisson's ratio is more resilient. Accordingly, when a material having a negative Poisson's ratio is subjected to stresses, such as those imposed upon a polishing pad during the polishing process, the material will display greater overall durability, longer life, and less deformation. Preferably, the material used to produce the polishing pads of the invention has a Poisson's ratio of from about –1 to less than 0 (e.g., from about –1 to about –0.1, from about –0.8 to about –0.2, or from about –0.6 to about –0.2).

[0010] Porous polymeric materials with negative Poisson's ratios desirably expand laterally when stretched and contract laterally when compressed. These unusual characteristics are achieved by forming the cells (i.e., pores) into a "re-entrant" shape, which bulges inwards and which unfolds under tension resulting in a lateral expansion. These cellular (i.e., porous) solids can be made from a variety of polymers or from metals. For a Poisson's ratio approaching -1, enhanced shear rigidity or high toughness is achieved.

[0011] The Poisson's ratio of the porous polymeric materials can be measured by any suitable means known in the art. For example, the Poisson's ratio for such porous polymeric materials can be measured by stretching the materials in an Instron machine using the method of ASTM D412-83 as described in Lakes et al., *J. Mat. Sci.*, *23*, 4406 (1988).

[0012] The polishing pad of the invention comprises, consists essentially of, or consists of any suitable material having a negative Poisson's ratio. Typically, the material having a negative Poisson's ratio comprises or is a polymer, which can be any suitable polymer, such as a thermoplastic polymer or a thermoset polymer. Preferably, the polymer is a thermoplastic polymer or a thermoset polymer selected from the group consisting of polyurethanes, cross-linked polyurethanes, polyolefins (e.g., polyethylenes, polypropylenes, cyclic polyolefins), cross-linked polyolefins, polyvinylalcohols, polyvinylacetates, polycarbonates, polyacrylic acids, polymethylmethacrylates, polyacrylamides, nylons, fluorocarbons, polyesters, polyethers, polyarylenes, polystyrenes, polyethyleneterephthalates, polyamides, polyimides, polyaramides, polytetrafluoroethylenes, polyetheretherketones, elastomeric rubbers, polyaromatics,

copolymers and block copolymers thereof, and mixtures and blends thereof. More preferably, the polymer resin is a thermoplastic polyurethane or polyolefin resin. Suitable porous polymeric materials with a negative Poisson's ratio are described in Lakes, *Science*, *235*, 1035 (1987), and U.S. Patent 4,668,557.

[0013] The polishing pad of the invention desirably has a density of about 1 g/cm^3 or less (e.g., about 0.8 g/cm^3 or less, about 0.6 g/cm^3 or less, about 0.4 g/cm^3 or less, or about 0.2 g/cm^3). The polishing pad of the invention desirably has a density of about 0.01 g/cm^3 or more (e.g., about 0.02 g/cm^3 or more, about 0.05 g/cm^3 or more, or about 0.08 g/cm^3 or more). In addition, the polishing pad of the invention preferably has a void volume of about 75% or less (e.g., about 50 % or less, about 40% or less, or about 30% or less). The polishing pad of the invention desirably has a void volume of about 1% or more (e.g., about 2% or more, about 5% or more, or about 10% or more).

[0014] The polishing pad of the invention, desirably, has a pore density of greater than about 10 pores/cm (e.g., greater than about 15 pores/cm, greater than about 20 pores/cm, or greater than about 30 pores/cm). The polishing pad of the present invention typically has an average pore diameter of about 2500 μm or less (e.g., about 2000 μm or less, about 1500 μm or less, about 1000 μm or less). The polishing pad of the invention also typically has an average pore diameter of about 0.1 μm or more (e.g., about 0.5 μm or more, about 1 μm or more, about 5 μm or more, or about 10 μm or more).

[0015] The polishing pad of the invention typically comprises a polishing surface, which contacts a workpiece when used to polish the workpiece. The polishing surface of the polishing pad optionally further comprises regions of different density, porosity, hardness, modulus, and/or compressibility. The different regions can have any suitable shape or dimension. Typically, the regions of contrasting density, porosity, hardness, and/or compressibility are formed on the polishing pad by an *ex situ* process (i.e., after the polishing pad is formed).

[0016] The polishing pad of the invention optionally further comprises grooves, channels, and/or perforations. Such features can facilitate the lateral transport of a polishing composition across the surface of the polishing pad. The grooves, channels, and/or perforations can be in any suitable pattern and can have any suitable depth and width. The polishing pad can have two or more different groove patterns, for example a combination of large grooves and small grooves as described in U.S. Patent 5,489,233. The grooves can be in the form of linear grooves, slanted grooves, concentric grooves, spiral or circular grooves, or XY crosshatch pattern, and can be continuous or non-continuous in connectivity.

[0017] The polishing pad of the invention optionally can be modified by buffing or conditioning, such as by moving the pad against an abrasive surface. The preferred abrasive

surface for conditioning is a disk which is preferably metal and which is preferably embedded with diamonds of a size in the range of 1 μm to 0.5 mm. Optionally, conditioning can be conducted in the presence of a conditioning fluid, preferably a water-based fluid containing abrasive particles.

[0018] The polishing pad of the invention can be used alone, or optionally can be mated to another polishing pad. When two polishing pads are mated, the polishing pad intended to contact the substrate or work piece to be polished serves as the polishing layer, while the other polishing pad serves as the subpad. For example, the polishing pad of the invention can be a subpad that is mated to a conventional polishing pad having a polishing surface, wherein the conventional polishing pad serves as the polishing layer. Alternatively, the polishing pad of the invention can comprise a polishing surface, and serve as the polishing layer, and can be mated to a conventional polishing pad that serves as a subpad. Suitable polishing pads for use as the polishing layer in combination with a polishing pad of the invention include solid or porous polyurethane pads, many of which are well known in the art. Suitable subpads include polyurethane foam subpads (e.g., Poron® foam subpads from Rogers Corporation), impregnated felt subpads, microporous polyurethane subpads, or sintered urethane subpads. In addition, the polishing pad and the subpad can comprise the same or different materials and can both comprise re-entrant materials that are the same or different. The polishing layer and/or the subpad optionally comprises grooves, channels, hollow sections, windows, apertures, and the like. The subpad can be affixed to the polishing layer by any suitable means. For example, the polishing layer and subpad can be affixed through adhesives or can be attached via welding or similar technique. Typically, an intermediate backing layer such as a polyethyleneterephthalate film is disposed between the polishing layer and the subpad. When the polishing pad of the invention is mated to a conventional polishing pad, the composite polishing pad also is considered a polishing pad of the invention.

[0019] The polishing pad of the invention optionally further comprises one or more apertures, transparent regions, or translucent regions (e.g., windows as described in U.S. Patent 5,893,796). The inclusion of such apertures or translucent regions (i.e., optically transmissive regions) is desirable when the polishing pad is to be used in conjunction with an *in situ* CMP process monitoring technique. The aperture can have any suitable shape and may be used in combination with drainage channels for minimizing or eliminating excess polishing composition on the polishing surface. The translucent region or window can be any suitable window, many of which are known in the art. For example, the translucent region can comprise a glass or polymer-based plug that is inserted in an aperture of the polishing pad or may comprise the same polymeric material used in the remainder of the polishing pad. Typically, the translucent regions have a light transmittance of about 10% or

more (e.g., about 20% or more, or about 30% or more) at one or more wavelengths between from about 190 nm to about 10,000 nm (e.g., from about 190 nm to about 3500 nm, from about 200 nm to about 1000 nm, or from about 200 nm to about 780 nm).

[0020] The transparent window portion can have any suitable structure (e.g., crystallinity), density, and porosity. For example, the transparent window portion can be solid or porous (e.g., microporous or nanoporous having an average pore size of less than 1 μm). Preferably, the transparent window portion is solid or is nearly solid (e.g., has a void volume of about 3% or less). The transparent window portion optionally further comprises particles selected from polymer particles, inorganic particles, and combinations thereof. The transparent window portion optionally contains pores.

[0021] The transparent window portion optionally further comprises a dye, which enables the polishing pad material to selectively transmit light of a particular wavelength(s). The dye acts to filter out undesired wavelengths of light (e.g., background light) and thus improves the signal to noise ratio of detection. The transparent window portion can comprise any suitable dye or may comprise a combination of dyes. Suitable dyes include polymethine dyes, di-and tri-arylmethine dyes, aza analogues of diarylmethine dyes, aza (18) annulene dyes, natural dyes, nitro dyes, nitroso dyes, azo dyes, anthraquinone dyes, sulfur dyes, and the like. Desirably, the transmission spectrum of the dye matches or overlaps with the wavelength of light used for *in situ* endpoint detection. For example, when the light source for the endpoint detection (EPD) system is a HeNe laser, which produces visible light having a wavelength of about 633 nm, the dye preferably is a red dye, which is capable of transmitting light having a wavelength of about 633 nm.

[0022] The polishing pad of the invention optionally contains particles, e.g., particles that are incorporated into the pad. The particles can be abrasive particles, polymer particles, composite particles (e.g., encapsulated particles), organic particles, inorganic particles, clarifying particles, water-soluble particles, and mixtures thereof. The polymer particles, composite particles, organic particles, inorganic particles, clarifying particles, and water-soluble particles also may be abrasive, or may be non-abrasive, in nature.

[0023] The abrasive particles can be of any suitable material. For example, the abrasive particles can comprise a metal oxide, such as a metal oxide selected from the group consisting of alumina, silica, titania, ceria, zirconia, germania, magnesia, co-formed products thereof, and combinations thereof, or a silicon carbide, boron nitride, diamond, garnet, or ceramic abrasive material. The abrasive particles can be hybrids of metal oxides and ceramics or hybrids of inorganic and organic materials. The particles also can be polymer particles many of which are described in U.S. Patent 5,314,512, such as polystyrene particles, polymethylmethacrylate particles, liquid crystalline polymers (LCP, e.g., Vectra® polymers from Ciba Geigy), polyetheretherketones (PEEK's), particulate

thermoplastic polymers (e.g., particulate thermoplastic polyurethane), particulate cross-linked polymers (e.g., particulate cross-linked polyurethane or polyepoxide), or a combination thereof. If the porous re-entrant material comprises a polymer resin, then the polymer particle desirably has a melting point that is higher than the melting point of the polymer resin of the porous foam. The composite particles can be any suitable particle containing a core and an outer coating. For example, the composite particles can contain a solid core (e.g., a metal oxide, metal, ceramic, or polymer) and a polymeric shell (e.g., polyurethane, nylon, or polyethylene). The clarifying particles can be phyllosilicates, (e.g., micas such as fluorinated micas, and clays such as talc, kaolinite, montmorillonite, hectorite), glass fibers, glass beads, diamond particles, carbon fibers, and the like.

[0024] The polishing pad of the invention can be produced by any suitable means known in the art. For example, the polishing pad can be produced directly from a porous polymeric material having a negative Poisson's ratio. Alternatively, the polishing pad comprising a porous polymeric material having a negative Poisson's ratio can be produced from a conventional open-cell material, closed-cell material, or a combination thereof by causing the cell walls of each cell (i.e., pore) to permanently protrude inward, resulting in a "re-entrant" (i.e., convex) structure. For example, specimens of conventional porous polymeric materials (e.g., polymeric materials having a positive Poisson's ratio) can be compressed triaxially (i.e., in three orthogonal directions) and placed in a mold. The mold is heated to a temperature slightly above the softening temperature of the porous polymeric material. The mold is then cooled under volumetric strain, and the re-entrant material is extracted. One such means for making a porous polymeric material having a negative Poisson's ratio for use in producing the polishing pad of the invention is described by Lakes, *Science*, *235*, 1038 (1987). The conventional porous polymeric material can be produced by any means known in the art. Such methods include foaming a polymer sheet in the presence of a supercritical gas.

[0025] The polishing pad of the invention is particularly suited for use in conjunction with a chemical-mechanical polishing (CMP) apparatus. Typically, the apparatus comprises (a) a platen, which, when in use, is in motion and has a velocity that results from orbital, linear, or circular motion, (b) a polishing pad of the invention in contact with the platen and moving with the platen when in motion, and (c) a carrier that holds a workpiece to be polished by contacting and moving relative to the surface of the polishing pad intended to contact a workpiece to be polished. The polishing of the workpiece takes place by the workpiece being placed in contact with the polishing pad and then the polishing pad moving relative to the workpiece, typically with a polishing composition therebetween, so as to abrade at least a portion of the workpiece to polish the workpiece. The CMP apparatus can

be any suitable CMP apparatus, many of which are known in the art. The polishing pad of the invention also can be used with linear polishing tools.

[0026] The polishing pad of the invention can display superior toughness and tear resistance because of the high extensibility of the material having a negative Poisson's ratio. The materials having a negative Poisson's ratio can provide superior acoustic and vibration damping capability due to vibration absorption by the convex (i.e., re-entrant) shape of the cell walls (i.e., pore walls). This damping acts as an elastic impact force buffer and typically will better distribute stress and help to improve edge-on effects seen in workpieces during chemical-mechanical polishing.

[0027] Suitable workpieces that can be polished with the polishing pad of the invention include memory storage devices, glass substrates, memory or rigid disks, metals (e.g., noble metals), magnetic heads, inter-layer dielectric (ILD) layers, polymeric films, low and high dielectric constant films, ferroelectrics, micro-electro-mechanical systems (MEMS), semiconductor wafers, field emission displays, and other microelectronic workpieces, especially microelectronic workpieces comprising insulating layers (e.g., metal oxide, silicon nitride, or low dielectric materials) and/or metal-containing layers (e.g., copper, tantalum, tungsten, aluminum, nickel, titanium, platinum, ruthenium, rhodium, iridium, silver, gold, alloys thereof, and mixtures thereof). The term "memory or rigid disk" refers to any magnetic disk, hard disk, rigid disk, or memory disk for retaining information in electromagnetic form. Memory or rigid disks typically have a surface that comprises nickel-phosphorus, but the surface can comprise any other suitable material. Suitable metal oxide insulating layers include, for example, alumina, silica, titania, ceria, zirconia, germania, magnesia, and combinations thereof. In addition, the workpiece can comprise, consist essentially of, or consist of any suitable metal composite. Suitable metal composites include, for example, metal nitrides (e.g., tantalum nitride, titanium nitride, and tungsten nitride), metal carbides (e.g., silicon carbide and tungsten carbide), nickel-phosphorus, alumino-borosilicate, borosilicate glass, phosphosilicate glass (PSG), borophosphosilicate glass (BPSG), silicon/germanium alloys, and silicon/germanium/ carbon alloys. The workpiece also can comprise, consist essentially of, or consist of any suitable semiconductor base material. Suitable semiconductor base materials include single-crystal silicon, poly-crystalline silicon, amorphous silicon, silicon-on-insulator, and gallium arsenide. Preferably, the workpiece comprises a metal layer, more preferably a metal layer selected from the group consisting of copper, tungsten, tantalum, platinum, aluminum, and combinations thereof. Even more preferably, the metal layer comprises copper.

[0028] The polishing composition of the polishing system that can be used with the polishing pad of the invention typically comprises a liquid carrier (e.g., water) and optionally one or more additives selected from the group consisting of abrasives (e.g.,

alumina, silica, titania, ceria, zirconia, germania, magnesia, and combinations thereof), oxidizers (e.g., hydrogen peroxide and ammonium persulfate), corrosion inhibitors (e.g., benzotriazole), film-forming agents (e.g., polyacrylic acid and polystyrenesulfonic acid), complexing agents (e.g., mono-, di-, and poly-carboxylic acids, phosphonic acids, and sulfonic acids), pH adjustors (e.g., hydrochloric acid, sulfuric acid, phosphoric acid, sodium hydroxide, potassium hydroxide, and ammonium hydroxide), buffering agents (e.g., phosphate buffers, acetate buffers, and sulfate buffers), surfactants (e.g., nonionic surfactants), salts thereof, and combinations thereof. The selection of the components of the polishing composition depends in part on the type of workpiece being polished.

[0029] Desirably, the CMP apparatus further comprises an *in situ* polishing endpoint detection system, many of which are known in the art. Techniques for inspecting and monitoring the polishing process by analyzing light or other radiation reflected from a surface of the workpiece are known in the art. Such methods are described, for example, in U.S. Patent 5,196,353, U.S. Patent 5,433,651, U.S. Patent 5,609,511, U.S. Patent 5,643,046, U.S. Patent 5,658,183, U.S. Patent 5,730,642, U.S. Patent 5,838,447, U.S. Patent 5,872,633, U.S. Patent 5,893,796, U.S. Patent 5,949,927, and U.S. Patent 5,964,643. Desirably, the inspection or monitoring of the progress of the polishing process with respect to a workpiece being polished enables the determination of the polishing end-point, i.e., the determination of when to terminate the polishing process with respect to a particular workpiece.

[0030] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

[0031] The use of the terms "a" and "an" and "the" and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms "comprising," "having," "including," and "containing" are to be construed as open-ended terms (i.e., meaning "including, but not limited to,") unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise

claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

[0032] Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.